One-step synthesis of shelled PbS nanoparticles in a layered double hydroxide matrix

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The one-step preparation of capped PbS nanoparticles in an inorganic matrix *via* UV-induced decomposition of lead thiosulfate complexes intercalated into a hydrotalcite-type layered double hydroxide is reported.

Semiconductor nanoparticles or 'quantum dots' have recently attracted particular attention due to their unique electronic and optical properties.[1,2] 'Core-shell' semiconductor nanocomposites possess important advantages over nanoparticles capped with organic ligands. First, they show enhanced chemical stability and stability against photodegradation since organic species are weakly bound to nanocrystal surface atoms.[3] Second, variation of the type and thickness of the shell material provides additional control over the electronic structure of nanocrystals and enables one to tune up their optical and electric properties.[4]
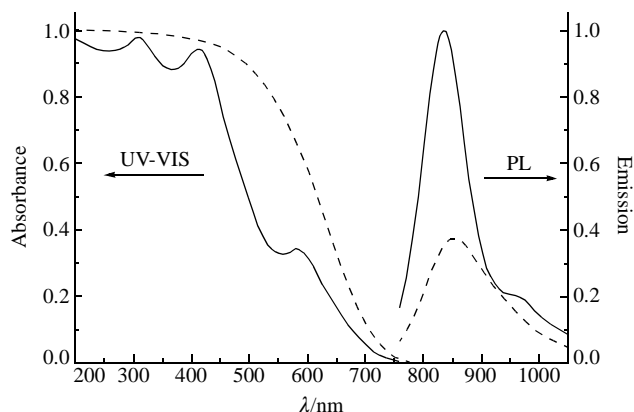
Figure 1 UV-VIS and PL spectra of PbS/LDH nanocomposites prepared by heating at 200 °C (dashed lines) and UV irradiation (solid lines).

Figure 2 TEM images of PbS nanoparticles incorporated into an LDH matrix. (*a*), (*b*) Composite prepared by heating at 200 °C. (*c*), (*d*) Composite prepared by UV irradiation.

Here we report the one-step formation of capped lead sulfide nanoparticles by decomposition of Pb^{II} anionic complexes intercalated into the interlayer space of hydrotalcite-like layered double hydroxides (LDH).

Layered double hydroxides have the general formula $M'_{1-x}M''_x(OH)_2[(anion)_{x/n}\cdot mH_2O]$, where M′ and M″ are metals in oxidation states of +2 and +3, respectively, and anion^{n−} is virtually any inorganic or organic anion. Their structure consists of positively charged hydroxide layers $[M'_{1-x}M''_x(OH)_2]^{x+}$, which are bonded by negatively charged anions arranged in the interlayer space. Due to a relatively large interlayer distance, anions in LDHs are readily exchangeable, and it is possible to obtain species with a stoichiometric content of an appropriate anion^{n−}. When anion^{n−} undergoes a chemical transformation, hydroxide layers of LDH restrict the reaction area. Thus, the interlayer space of LDH may serve as a two-dimensional nanoreactor.

Nanoparticulate PbS in various matrices is usually prepared *via* sulfidation of Pb^{II}-containing species by gaseous H_2S or Na_2S.[5] However, this process is essentially exothermic, which may result in a broad particle-size distribution or aggregation of the particles. Sometimes, the formation of PbS occurs as a result of decomposition of a lead complex with a sulfidising ligand, *e.g.*, dithiocarbamate.[6] In order to perform the synthesis of PbS in the interlayer space of LDH, one should choose a sulfur-containing anionic complex of lead that undergoes decomposition giving lead sulfide as a solid product. One compound, which meets the above condition, is the thiosulfate complex $[Pb(S_2O_3)_2]^{2-}$ [its preparation can be achieved by the interaction of lead(II) nitrate with sodium thiosulfate].

As a precursor compound, we used the nitrate form of MgAl LDH $\{Mg_3Al(OH)_8[NO_3]\}$ prepared as described previously.[7] The synthesis of $Mg_3Al(OH)_8\{[Pb(S_2O_3)_2]^{2-}_{0.5}\}$ was performed by exchanging NO_3^- in $Mg_3Al(OH)_8[NO_3]$ for $[Pb(S_2O_3)_2]^{2-}$ in an aqueous solution of $Na_2[Pb(S_2O_3)_2]$. The XRD analysis of the samples showed that all LDHs are single phases with maxima characteristic of hydrotalcite-like LDHs. The cell parameters c are 26.81±0.03 and 28.21±0.04 Å for the nitrate and thiosulfate forms of LDHs, respectively. The last step of the synthesis was the decomposition of $Mg_3Al(OH)_8\{[Pb(S_2O_3)_2]_{0.5}\}$. We used two methods for the preparation of PbS: UV irradiation and thermal decomposition at 200 °C. UV irradiation was carried out using a Spectron-1860 2000 W UV lamp for 10 h. Liquid nitrogen ($T = 77$ K) was used to cool the sample during the synthesis. Thermal decomposition was performed in an air-free atmosphere because of the possibility of oxidation of the nanocrystalline PbS. Note that heating at 200 °C may result in partial destruction of LDH due to dehydration.[8] The XRD patterns of the prepared samples show that both of them contain nanocrystalline PbS. In the case of thermal decomposition, broad maxima at $2\theta \sim 37°$, 43° and 62.3° indicate the presence of MgO, which appears as a result of thermal dehydration of the LDH phase. An LDH phase with the lattice parameter $c = 22.87±0.03$ Å, which corresponds to CO_3^{2-}-substituted MgAl
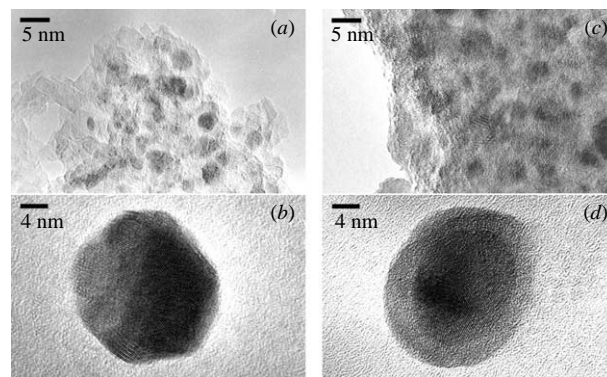
LDH (ICDD-70-2151), was also observed. IR spectroscopy also confirms the presence of carbonate anions (bands at 1361 and 855 cm^{−1}). The presence of the carbonate form of LDH is explained by partial rehydration and recarbonization of defect MgO in air.[9] The XRD spectrum of the sample prepared by UV irradiation contains well-defined maxima of PbS and LDH. No other phases are observed. LDH reflections are broader than those of the precursor. The lattice parameter c calculated from the XRD data is $c = 27.03±0.06$ Å. Since the decomposition of $[Pb(S_2O_3)]^{2-}$ occurs according to the reaction

$$[Pb(S_2O_3)]^{2-} \rightarrow PbS\downarrow + S\downarrow + SO_2\uparrow + SO_4^{2-},$$
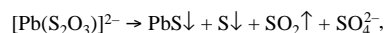
it is reasonable to expect that the sulfate ion will replace lead thiosulfate in the interlayer space of the LDH. Indeed, the measured value of c corresponds to the lattice parameter of SO_4^{2-}-substituted LDH ($c = 26.9$ Å according to ref. 10).

Figure 1 compares the UV-VIS spectra of samples prepared by thermal decomposition and UV irradiation. Both of the spectra show a blue shift typical of nanoparticulate PbS. The particle size R can be estimated using the following equation for the shift of the bandgap:[11]

$$E = E_g + \hbar_2\pi_2/2\mu R^2, \qquad (1)$$

where E is the bandgap for a nanoparticulate semiconductor, E_g is the bandgap for the bulk material, and μ is the reduced mass of the exciton. Calculations according to equation (1) show that the size of the PbS particles is around ~4.5 nm for the sample obtained at $T = 200$ °C and ~4 nm for the UV-irradiated sample.

The UV-VIS spectrum of the sample obtained by UV irradiation shows additional peaks at 580, 400 and 300 nm. These peaks correspond to the $1S_e–1S_h$, $1S_e–1P_h$ and $1S_h–1P_e$ exciton transitions in PbS, respectively.[12] These transitions are normally not observed in the UV-VIS spectra of nanocrystalline PbS. However, such transitions were observed earlier for PbS nanoparticles prepared in the presence of poly(vinyl alcohol).[13] Another example of exciton transitions in absorption spectra of nanocrystalline PbS has been reported by Patel *et al.*[14] In this work, the surface of PbS nanoparticles was modified by DNA molecules. It is generally accepted[15] that the presence of the forbidden exciton transitions in the spectra of PbS should be attributed to a surface modification of nanoparticles.

Also shown in Figure 1 are the photoluminescence (PL) spectra of the samples. Each PL spectrum consists of two peaks at $\lambda = 840$ and 910–940 nm. The former peak corresponds to the band-edge luminescence and the latter peak, to luminescence from the surface trap sites. The intensity of the band edge luminescence for the sample obtained by UV-irradiation is approximately four times higher than that of the sample obtained by heating at 200 °C.

The difference between the products of UV and thermal decomposition of $[Pb(S_2O_3)_2]^{2-}$ inside the LDH matrix was further studied by transmission electron microscopy. Figure 2 compares the TEM images of two samples. The particle size is in the range 3–5 nm for both of the samples. Occasionally, larger

particles (up to 20 nm) can be found. Direct measurements of interplanar distances in TEM images, as well as electron diffraction studies, confirm the presence of cubic PbS crystals with the lattice parameter *a* corresponding to stoichiometric lead sulfate ($a = 5.93\pm0.02$ Å for both samples).

A more detailed examination of the particles obtained by UV decomposition shows that they have amorphous shells [Figure 2(*d*)]. The shells probably consist of elemental sulfur, which is formed during the decomposition of $[Pb(S_2O_3)_2]^{2-}$ at a low temperature according to equation (1). No shells are observed in the case of thermal decomposition [Figure 2(*b*)]. A possible reason for the absence of the shells in this case is that the decomposition is performed at a temperature above the melting point of elemental sulfur ($T_m = 98$ °C).

In conclusion, UV irradiation of $[Pb(S_2O_3)_2]^{2-}$-substituted MgAl LDH provides a one-step synthesis of core-shell PbS/S nanoparticles. The presence of amorphous shells affects the optical properties of the nanocrystals, probably, due to a surface modification. The use of $Mg_{1-x}Al_x(OH)_2\{[Pb(S_2O_3)_2^{2-}]_{x/2}\cdot mH_2O\}$ precursors enables one to precisely control the load of the nanoparticles in the solid state matrix by simply controlling the Mg:Al ratio in the initial LDH. This control is important for creating quantum dot-based optical devices.

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